

PATENT SPECIFICATION

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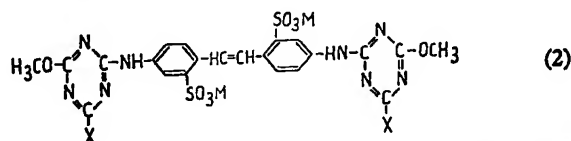
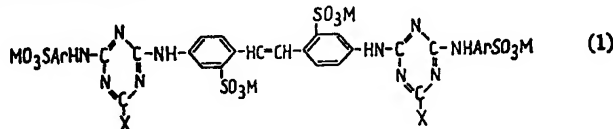


(54) AN OPTICAL BRIGHTENING AGENT AND PROCESS FOR THE PREPARATION OF SAME

(71) We, INSTYTUT PRZEMYSŁU ORGANICZNEGO, of Warszawa, Annopol Street 6, Poland, a state enterprise organised and existing under the laws of Poland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an optical brightening agent and to the process for the preparation thereof. This brightening agent is designed for increasing the brightness of, particularly cellulosic or polyamide fabrics and papers.

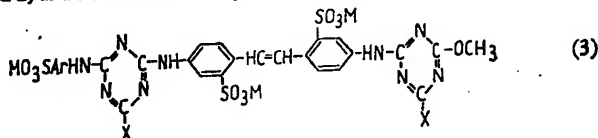
A previously proposed optical brightening agent contained as the active substance a compound of formula 1 or 2



where X is an amino group or an amino-substituted aliphatic, aromatic or heterocyclic group, Ar is a *m*- or *p*-phenylene group, and M is a monovalent cation. This brightening agent, although having good brightening properties, is relatively expensive to prepare because of the high price of the raw materials. The high price of the optical brightening agent may be acceptable if the brightening properties and especially the degree of the whiteness produced is exceptional.

An object of this invention is to provide an optical brightening agent which is superior to known products in respect of the maximum degree and purity of the whiteness.

According to the present invention there is provided an optical brightening agent comprising a composition containing as active components either or both of compounds of formulae 1 and 2, and in addition a compound of formula 3



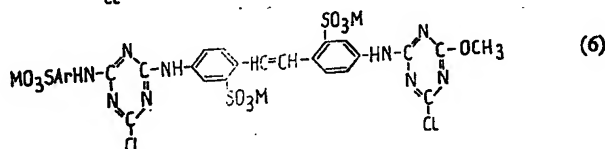
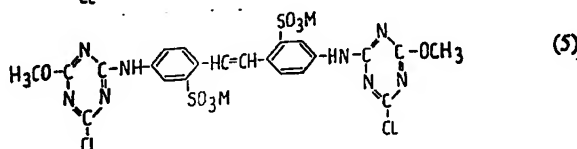
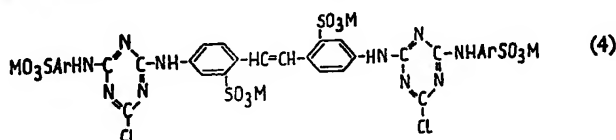
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where Ar is a *m*- or *p*-phenylene group, X is a radical of an aliphatic, aromatic or heterocyclic amine or a —NH_2 group and M is a monovalent cation.

Preferably the agent contains a compound of the formula 3 in a quantity amounting from 20 to 65 parts by weight per 100 parts by weight of the total of the active components.

When the optical brightening agent is a two component mixture containing the compound of formula 3 and either the compound of formula 1 or the compound of formula 2, defined above, it may be prepared by simply mixing the individual components. On the other hand, if optical brightening agent is a three component mixture containing the compound of formula 3 and both of the compounds of formula 1 and 2 it may be prepared by a convenient chemical process.

According to the invention, the said process for preparing an optical brightening agent having three components comprising the compounds of the formulae 1, 2 and 3 defined above, comprises condensing a mixture of 2-methoxy-4,6-dichloro-*sym*-triazine and 4,6-dichloro-2(*m*-sulphophenylamino)-*sym*-triazine or its sodium salt or 4,6-dichloro-2(*p*-sulphophenylamino)-*sym*-triazine or its sodium salt with 4,4'-diaminostilbene-2,2'-disulphonic acid or its disodium salt, to obtain an intermediate product comprising a mixture of compounds of formulae 4, 5 and 6



where Ar and M are as defined above, and condensing said intermediate product with an aliphatic, aromatic or heterocyclic amine or with ammonia.

For the reaction it is preferable to use per 1 mol of 4,4'-diaminostilbene-2,2'-disulphonic acid or its disodium salt, from 0.5 to 1.5 mol, advantageously from 0.85 to 1.15 mol of 2-methoxy-4,6-dichloro-*sym*-triazine and from 0.5 to 1.5 mol, advantageously from 0.85 to 1.15 mol of 4,6-dichloro-2(*m*- or *p*-sulphophenylamino)-*sym*-triazine, the total quantity of these two triazines amounting from 1.9 to 2.3 mol. For each 1 mol of the total amount of the intermediate product comprising a mixture of compounds of the formulae 4, 5 and 6, it is preferred to use at least 2.3 mol of aromatic amine or at least 3 mol of aliphatic or heterocyclic amine or at least 6 mol of ammonia. The reaction product obtained may then be treated with sodium chloride or with mineral acid, such as hydrochloric acid, or with an organic acid, such as acetic acid, then the mixture is filtered, and the paste obtained is dried in any drying apparatus or it is converted by a known method into liquid form, such as a solution, or into a suspension.

The optical brightening agent of this invention gives excellent effects on the whiteness of fabrics treated therewith, particularly on products made of fibres of natural or regenerated cellulose, on products made of polyamide fibres, and on paper products. Said agent brightens the cellulosic fibres to a considerably higher degree than previous optical brightening agents such as mixtures of compounds of the formulae 1 or 2, which have up to now been generally considered as the most effective products. For example cotton fabric brightened by means of the compound of the formula 1, where Ar is an *m*-phenylene group, X is a diethanolamino group, and M is a sodium cation, a maximum whiteness degree of 131 defined according to the Anni-Berger formula is obtained (Die Farbe 1959 8, 187). When using the compound of the formula 2, where X is a diethanolamino group and M is a sodium cation, a

maximum whiteness degree of 135 is obtained. The compound of formula 3, brightness to a maximum whiteness degree of 136. On the other hand, a same fabric brightened in the same conditions with the optical brightening agent of the invention and obtained according to the invention method, containing as the active substance 67 parts by weight of compounds of the formulae 1 and 2, and 33 parts by weight of the compound of the formula 3, a maximum whiteness degree of 140 is obtained. The tinge of the fabric thus brightened is more blue, more bright and more pure than in the case of using any individual compound of the formulae 1, 2 or 3.

The invention will now be described, by way of illustration, in the following Examples.

Example I

An optical brightening agent containing 67 parts by total weight of the compounds of formulae 1 and 2, where Ar is an *m*-phenylene group, X is a $-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ group, and M is a sodium cation; and 33 parts by weight of the compound of the formula 3, where Ar, X and M are the same as in formula 1 and 2, is used for increasing the whiteness degree of the fabric made of mercerized cotton fibre.

The brightening of the fabric is carried out in the following manner. Into a bath containing 20 kg of sodium chloride, 1 kg of sodium carbonate and 0.3 kg of the optical brightening agent in 4 m³ of water, 100 kg of fabric are introduced. The whole is heated to a temperature of 40°C, and then, after 30 minutes, the fabric is removed from the bath, rinsed and dried.

After this treatment the fabric becomes a bright and pure white of blue tinge. The whiteness degree of the brightened fabric, defined according to the Anni-Berger formula, amounts to 140°.

The optical brightening agent stated in this Example is obtained in the following manner. Into a reactor containing 1 m³ of methanol and 560 kg of sodium bicarbonate, 250 kg of cyanuric chloride are introduced. The whole is stirred for 2.5 hours at a temperature of 12°C. As a result of the process, 4,6-dichloro-2-methoxy-sym-triazine is formed. At the same time, into separate reactor 6 m³ of water, 2000 kg of ice, 5 kg of a surface-active agent (being the condensation product of 1 mol of fatty alcohol with 18 mol of ethylene oxide), 250 kg of cyanuric chloride and 228 kg of metanilic acid are successively introduced. Then the whole is stirred for 1.5 to 2.5 hours till disappearance of the aromatic amine in the reacting mixture, maintaining at this time a temperature of from 0 to 5°C and dosing simultaneously a 10% aqueous sodium carbonate solution for the purpose of neutralizing the hydrogen chloride evolved during the reaction. The result of the reaction is 4,6-dichloro-2-(*m*-sulphophenyl-amino)-sym-triazine. The two sym-triazine derivatives obtained are decanted into one reactor without separation from the reaction mixture. To the mixture obtained, 515 kg of disodium salt of 4,4'-diaminostilbene-2,2'-disulphonic acid are added and the mixture is stirred for 30 minutes at a temperature of from 0 to 5°C, whereupon it is heated for 1 hour to a temperature of 20°C and is stirred at this temperature till the end of the reaction. The result of the reaction is an intermediate product constituting a mixture of compounds of the formulae 4, 5 and 6, in which Ar is a *m*-phenylene-group, and M is a sodium cation. To the mixture obtained, 540 kg of diethanolamine are added and the whole is stirred for 2 hours at a temperature of 90°C. After this time, the solution obtained is filtered, to the filtrate sodium chloride in a quantity of 20% weight/volume ratio in relation to the volume of the liquid is added, the mixture is then cooled to a temperature of 25°C, stirred for 3 hours, filtered, and the paste obtained is dried in a spray drier. There are obtained 1350 kg of a light-yellow product which does not melt up to a temperature of 300°C. Its composition is as defined in the first paragraph of this Example.

Example II

An optical brightening agent containing as the active substance 67 parts by weight of compounds of the formulae 1 and 2, where Ar is an *m*-phenylene group, X is a $-\text{NHCH}_2\text{CH}_2\text{OH}$ group, and M is a sodium cation, and 33 parts by weight of the compound of the formula 3, where Ar, X and M are the same as for formulae 1 and 2, is used for increasing the whiteness degree of the cotton fabric during the high-grade finish. The brightening of the fabric takes place as follows. The chemically bleached fabric made of mercerized cotton fibres is padded with a finishing liquid composed of: cycloethylene urea formaldehyde resin sold by the Trade Mark Silezjan EM—5 kg, polyacrylic resin sold by the Trade Mark Perapret HV—1.5 kg, urea—1 kg, hexahydrate magnesium chloride—1 kg, the above-mentioned optical brightening agent—0.3 kg and water—92 dm³.

The padded fabric is then allowed to pass between wringing rolls, leaving in the fabric liquid in a quantity equal in weight to the weight of dry fibres, and is subjected to the action of hot air of a temperature of 145°C for 5 minutes. After this treatment the fabric becomes a bright and pure white with a blue tinge and reaches a whiteness degree of 138.

The optical brightening agent used in this Example is obtained in the following manner. Into the intermediate reaction product constituting a mixture of compounds of the formulae 4, 5 and 6, and obtained in the manner described in Example 1, 410 kg of monoethanolamine are introduced and the whole is stirred at a temperature of 85°C for 2 hours. The solution obtained is then filtered, sodium chloride in a quantity of 16% by weight in relation to the volume of the liquid is added, then the mixture is cooled to a temperature of 25°C, is stirred for 3 hours, filtered and dried in a spray drier. There is obtained 1250 kg of a pale-yellow product which can be heated to 300°C without melting. The composition of the optical brightening agent obtained is stated in the first paragraph of this Example.

Example III

Chemically bleached fabric of mercerized cotton fibres is padded with a finishing liquid of the following composition: dibutyl phthalate modified polyvinyl acetate resin sold by the Trade Mark Winacet D-525—3 kg, ethylene oxide and stearic acid adduct sold under the Trade Mark Rokacet S-7—0.25 kg, optical brightening agent as in Example II—0.3 kg and water—96 dm³. Then the padded fabric is allowed to pass between wringing rolls, leaving in the fabric liquid in a quantity about equal in weight to the weight of dry fibres, whereupon the fabric is dried at a temperature of 100°C. After this treatment the fabric attains a whiteness degree of 148 and shows a bright blue-reddish tinge.

Example IV

An optical brightening agent containing as the active substance 67 parts by weight of compounds of the formulae 1 and 2, and 33 parts by weight of the compound of formula 3, where Ar is an *m*-phenylene group, X is a NH₂-group, and M is a sodium cation, is used for brightening a fabric of viscose fibres. The high-grade finishing of the fabric is carried out in the following manner. Into the solution heated to a temperature of 50°C containing in 4 m³ of water, 20 kg of sodium chloride, 5 kg sodium carbonate and 0.8 kg of the optical brightening agent stated above, 100 kg of fabric made of viscose staple fibres are introduced, treatment being allowed to continue for 45 minutes. Then the fabric is rinsed and then dried at room temperature. After this treatment the fabric attains a whiteness degree of 131. When brightening the viscose fibre fabric with the aid of other, hitherto known optical brightening agents, it is not possible to obtain this whiteness degree.

The optical brightening agent stated in this Example is obtained in the following manner. Into the intermediate product of the reaction, constituting a mixture of compounds of the formulae 4, 5 and 6, and obtained in the same manner as in Example 1, 1 m³ of 25% ammonia solution is introduced, the whole is stirred for 4 hours at a temperature of 70°C and then the unreacted ammonia is distilled off with the steam. To the liquid remaining after the distillation of ammonia, sodium chloride is added in a quantity of 18% in relation to the volume of the mixture, which is then cooled to a temperature of 25°C, stirred for 3 hours, filtered, and the paste obtained is dried at a temperature of 80—90°C. One obtains about 1200 kg of a pale-yellow product which can be heated to 300°C without melting. Its composition is stated in the first paragraph of this Example.

Example V

An optical brightening agent, containing 77 parts by weight of compounds of the formulae 1 and 2, and 23 parts by weight of the compound of formula 3, where Ar is a *p*-phenylene group, X is a morpholine radical and M is a sodium cation, is used for increasing the whiteness degree of products made of polyamide fibres.

The brightening of the polyamide fibres is carried out in the following manner. In a solution heated to a temperature of 90°C, containing in 5 m³ of water, 2 dm³ of 100% acetic acid and 0.5 kg of the above-mentioned optical brightening agent, 100 kg of knitted fabric made of polycapraamide fibres are treated for 30 minutes. The knitted fabric is then rinsed and dried. The knitted fabric thus brightened exhibits a pure neutral tinge and a whiteness degree of 140.

The optical brightening agent stated in this Example is obtained in the following manner. Into the reactor there is successively introduced 5 m³ of water, 2000 kg of

ice, 3 kg of a non-ionic surface-active agent (a product of condensation of 1 mol of oleocetyl alcohol with 21 mol of ethylene oxide, and 375 kg of cyanuric chloride. Then, to the mixture obtained, a solution of 367 kg of sulphanilic acid sodium salt in 1.5 m³ of water is dosed over a period of 30 minutes and the whole is stirred till the aromatic amine in the reacting mixture is consumed, maintaining within this time a temperature of from 0 to 5°C and dosing simultaneously a 10% aqueous sodium carbonate solution for the purpose neutralizing the hydrogen chloride evolving during the reaction.

As a result of the reaction 4,6-dichloro-2(*p*-sulphophenylamino)-*sym*-triazine sodium salt is produced. Then, into the reactor 2-methoxy-4,6-dichloro-*sym*-triazine obtained from 125 kg of cyanuric chloride, 60 kg of sodium bicarbonate and 0.5 m³ of methanol in the manner as in Example 1 is introduced. To the mixture obtained a solution of 515 kg of disodium salt of 4,4'-diaminostilbene-2,2'-disulphonic acid in 4 m³ of water is dosed over a period of 1 hour and the whole is stirred at a temperature of from 0 to 10°C for 1 hour.

The contents of the reactor are then heated and stirred for 1.5 hours at a temperature of from 20 to 25°C, subsequently at a temperature of from 30 to 40°C until the aromatic amine in the reacting mixture is consumed. During this time a 10% aqueous sodium carbonate solution is dosed into the reactor for the purpose of neutralizing the hydrogen chloride evolving during the reaction.

The reaction produces an intermediate product comprising a mixture of compounds of the formulae 4, 5 and 6, where Ar is a *p*-phenylene group and M is a sodium cation. To the mixture obtained 450 kg of morpholine are added and the whole is stirred for 3 hours at a temperature of from 95 to 98°C. After this time, to the mixture obtained, sodium chloride is added in a quantity of 15% in relation to the volume of the liquid. Thereafter the mixture is cooled to a temperature of 25°, then stirred for 1 hour at this temperature, filtered and dried at a temperature of 85°C. About 1300 kg of a pale-yellow product which can be heated to 300°C without melting. Its composition is as stated in the first paragraph of this Example.

Example VI

Into a reactor 5 m³ of water, 2000 kg of ice, 3 kg of a surface-active agent—(product of condensation of 1 mol of oleocetyl alcohol with 21 mol of ethylene oxide) and 250 kg of cyanuric chloride are successively introduced. Then, to the suspension obtained, a solution of 246 kg of sulphanilic acid sodium salt in 1 m³ of water is dosed over a period of 30 minutes and the whole is stirred at a temperature of from 0 to 5°C until the aromatic amine in the reacting mixture is all consumed. A 10% aqueous sodium bicarbonate solution is dosed with stirring for the purpose of neutralizing the hydrogen chloride evolving during the reaction.

The process produces 4,6-dichloro-2(*p*-sulphophenylamino)-*sym*-triazine sodium salt. Then, into the reactor 2-methoxy-4,6-dichloro-*sym*-triazine obtained from 250 kg of cyanuric chloride, 350 kg of sodium bicarbonate and 1 m³ of methanol in the manner as in Example 1 are introduced.

To the mixture obtained 515 kg of disodium salt of 4,4'-diaminostilbene-2,2'-disulphonic acid are added and the mixture stirred for 30 minutes at a temperature of 3°C. It is then heated for 1 hour at a temperature of 25°C with continuous stirring to the end of the reaction. The reaction produces an intermediate product comprising a mixture of compounds of the formulae 4, 5 and 6, where Ar is a *p*-phenylene group, and M is a sodium cation.

Subsequently, into the reactor 300 kg of aniline are introduced, the whole is heated to a temperature of from 93° to 95°C and stirred at this temperature for 6 hours. After this time the mixture is rendered alkaline by means of sodium carbonate to a pH of 8.5. Sodium chloride in a quantity of 10% in relation to the volume of the liquid is then added and the mixture cooled to a temperature of 25°C, stirred for 2 hours, filtered and dried. About 1100 kg of a yellow product is obtained which can be heated to 300°C without melting. The obtained optical brightening agent contains as the active substance about 65 parts by weight of compounds of the formulae 1 and 2 as well as about 35 parts by weight of the compound of formula 3, where Ar is a *p*-phenylene-group, X is an aniline radical and M is a sodium cation. A fabric of viscose fibres brightened by means of this product as in Example IV attains a maximum whiteness degree of 133.

Example VII

An optical brightening agent containing as the active substance 35 parts by weight of the compound of formula 1, where Ar is a *p*-phenylene group, X is a $-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ group, and M is a triethanolammonium cation, and 65 parts by

weight of the compound of formula 3, where Ar is an *m*-phenylene group, X is a $-\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$ group, and M is a sodium cation, is used for increasing the whiteness degree of sized papers.

Paper brightening is carried out in the following manner. Into a hollander 7 m³ of water, 500 kg of chemically bleached cellulose and 4 kg of the above-mentioned optical brightening agent are introduced and the cellulose tearing process is carried out in the usual manner. Subsequently to the hollander 50 kg of kaolin, 8 kg of resin adhesive and aluminium sulphate are added to obtain a pH value of 4.5. After the components have been mixed, the whole is passed to the slice of the paper machine and the paper producing process is carried out in the usual manner. The paper obtained has a high whiteness degree amounting to 95%, determined on the "Elrepho" re-emission photometer.

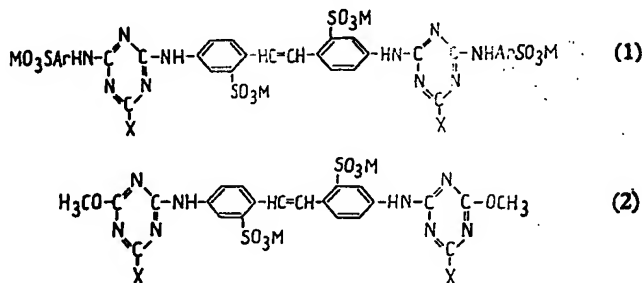
Example VIII

An optical brightening agent containing as the active substance 65 parts by weight of the compound of formula 2, where X is a $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ group, and M is a $[\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2]^+$ cation, and 35 parts by weight of the compound of formula 3, where Ar is an *m*-phenylene group, X is a $-\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$ group, and M is a $[\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2]^+$ cation, is used for increasing the whiteness degree of sized papers.

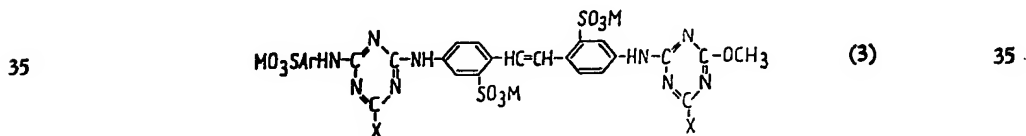
The method of brightening of the paper is carried out as follows. Into a hollander 7 m³ of water, 500 kg of chemically bleached cellulose and 4 kg of the above-mentioned optical brightening agent are introduced and the cellulose tearing process is carried out in the usual manner. Subsequently to the hollander are added 50 kg of kaolin, 8 kg of resin adhesive as well as aluminium sulphate to obtain a pH value of 4.5. After the components are thoroughly mixed, the mass is passed to the slice of the paper machine and the paper producing process is carried out in the usual manner. The paper obtained has a high whiteness degree which amounts to 96%, determined on the "Elrepho" re-emission photometer.

WHAT WE CLAIM IS:—

1. An optical brightening agent comprising a composition containing as active components either or both of compounds of formulae 1 and 2



and in addition a compound of formula 3

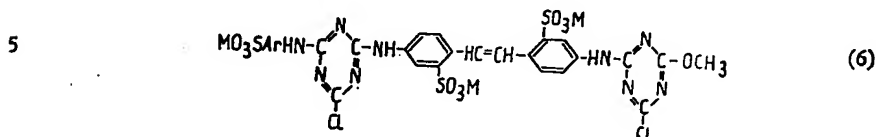
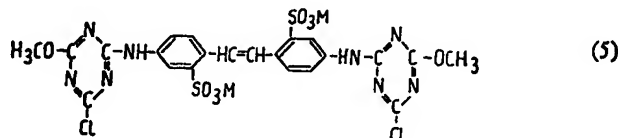
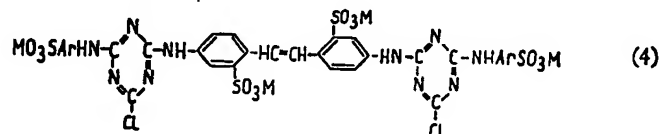


where Ar is a *m* or *p*-phenylene group, X is a radical of an aliphatic, aromatic or heterocyclic amine or a $-\text{NH}_2$ group and M is a monovalent cation.

2. An optical brightening agent as claimed in Claim 1, containing a compound of the formula 3 as defined in Claim 1, in a quantity amounting from 20 to 65 parts by weight of the active components.

3. A process for the preparation of an optical brightening agent comprising as active components the three compounds of the formulae 1, 2 and 3 as defined in Claim 1, comprising condensing a mixture of 2-methoxy-4,6-dichloro-*sym*-triazine and 4,6-dichloro-2-(*m*-sulphophenylamino)-*sym*-triazine, or its sodium salt, or 4,6-dichloro-2-(*p*-sulphophenylamino)-*sym*-triazine or its sodium salt with 4,4'-diaminostilbene-

2,2'-disulphonic acid or its disodium salt to form an intermediate product comprising a mixture of compounds of the formulae 4, 5 and 6



where Ar and M are as defined in Claim 1, and condensing with the intermediate product an aliphatic, aromatic or heterocyclic amine or with ammonia.

4. A process as claimed in Claim 3, in which for each 1 mol of 4,4'-diaminostilbene-2,2'-disulphonic acid, is reacted with from 0.5 to 1.5 mol of 2-methoxy-4,6-dichloro-*sym*-triazine and from 0.5 to 1.5 mol of 4,6-dichloro-2-(*m*-sulphophenylamino)-*sym*-triazine or its sodium salt, or 4,6-dichloro-2-(*p*-sulphophenylamino)-*sym*-triazine or its sodium salt, the total quantity of the two triazines amounting from 1.9 to 2.3 mol; and each 1 mol of the total amount of the intermediate product constituting a mixture of compounds of the formulae 4, 5 and 6 is reacted with at least 2.3 mol of aromatic amine or at least 3 mol of aliphatic amine or heterocyclic amine or at least 6 mol of ammonia.

5. A process as claimed in Claim 4, in which from 0.85 to 1.15 mol of 2-methoxy-4,6-dichloro-*sym*-triazine and from 0.85 to 1.15 of 4,6-dichloro-2-(*m*-sulphophenylamino)-*sym*-triazine or 4,6-dichloro-2-(*p*-sulphophenylamino)-*sym*-triazine are reacted with each mole of 4,4'-diaminostilbene-2,2'-disulphonic acid.

6. A process according to Claim 3 or 4 or 5, substantially as described in Examples I to VIII hereinbefore.

7. An optical brightening agent whenever prepared by the process claimed in any one of Claims 3 to 6.

8. A process of brightening fabrics comprising treating same with an optical brightening agent claimed in Claim 1 or Claim 2 or Claim 7.

9. A process according to Claim 8, substantially as hereinbefore described in Examples I to VIII.

10. Fabrics whenever treated by the process claimed in Claim 8 or Claim 9.

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